



## Article

# Application of Low Melting Metals for Separation of Uranium and Zirconium in a “Fused Chloride—Liquid Alloy” System

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**Abstract:** Closeness of electrochemical properties of uranium and zirconium makes separation of these metals in pyroelectrochemical reprocessing of spent nuclear fuels a challenging task. Varying electrode material can change metals' deposition potentials. The study was aimed at assessing the effect of the cathode material on deposition potentials of zirconium and uranium from 3LiCl–2KCl based melts. Solid (tungsten) and liquid (gallium, zinc, Ga–Zn, Ga–Sn and Ga–In alloy) working electrodes were tested at 532–637 °C. Galvanostatic cathodic polarization was employed and the applied cathodic current varied from 0.0001 to 1 A. Gallium–zinc eutectic alloy demonstrated the largest difference of zirconium and uranium deposition potentials. Zirconium/uranium separation factors were experimentally determined in a “molten salt—liquid metal” system for gallium and Ga–Zn eutectic based alloys.

**Keywords:** uranium; zirconium; low melting metals; separation; cathodic polarization; electrochemical deposition



**Citation:** Volkovich, V.A.; Maltsev, D.S.; Soldatova, M.N.; Ryzhov, A.A.; Ivanov, A.B. Application of Low Melting Metals for Separation of Uranium and Zirconium in a “Fused Chloride—Liquid Alloy” System.

*Metals* **2021**, *11*, 550. <https://doi.org/10.3390/met11040550>

Academic Editor: Gunter Gerbeth

Received: 2 March 2021

Accepted: 25 March 2021

Published: 28 March 2021

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## 1. Introduction

Currently nearly 440 nuclear power reactors are in operation in the world producing electricity. One of the ways of dealing with spent nuclear fuel (SNF) discharged from the reactors is reprocessing to return remaining (uranium) or newly formed (plutonium) fissile materials into the nuclear fuel cycle. Another goal of SNF reprocessing is separation of long living fission products or transuranium elements (neptunium, americium, curium) and preparing them for subsequent conversion into short living or stable nuclides, for example in a fast neutron reactor. Current industrial scale reprocessing is based on the solvent extraction (PUREX—plutonium uranium reduction extraction process). This technology is unable to process SNF with high burn-up and short cooling time due to radiolysis of water and organic extractants. Presence of neutron moderators (hydrogen and carbon) also limits the concentration of fissile nuclides in the solutions to ensure nuclear safety. SNF reprocessing in non-aqueous media can solve many problems intrinsic to the aqueous technologies. Pyrochemical reprocessing using molten salts and liquid metals as working media is currently considered as one of promising alternatives to the PUREX process. Molten salts and metals are stable towards radiation and absence of neutron moderators allows increasing concentration of fissile materials making the whole technology more compact. Separation of fissile materials from fission products in pyrochemical reprocessing can be achieved electrochemically or using exchange reactions in a “fused salt—liquid metal” system. Here liquid metals or alloys can act as reductive extractants for desired elements dissolved in a molten salt bath.

The electrode potential of zirconium in fused chlorides is more positive than uranium. Depending on temperature and cationic composition of the molten electrolyte, the standard apparent electrode potential of uranium equals to  $-(2.4\text{--}2.6)$  V vs. the standard chlorine reference electrode, and the standard apparent electrode potential of zirconium is around  $-(2.1\text{--}2.2)$  V. Of all fission product elements present in SNF, zirconium has the closest electrochemical properties to uranium and this makes separation of uranium and zirconium a difficult task. Concentration of zirconium in the technological electrolytes would be quite low compare to that of uranium resulting in greater shift of zirconium electrode potential to the negative values and bringing it even closer to uranium. Uranium and plutonium fission produces several zirconium isotopes [1] and SNF arriving for reprocessing can contain from 5 to 13 kg zirconium per ton (excluding fuel rods cladding). The exact amount of zirconium depends on the neutron spectrum in the reactor, nuclear fuel type, burnup and SNF cooling time.

Zirconium in alkali chloride-based melts can form stable ions in several oxidation states, +4 being the highest. First studies of electrochemical behavior of zirconium in fused alkali chlorides date back to the middle of the last century. However, there is still some controversy concerning the mechanism of Zr(IV) ions reduction and stable oxidation states of zirconium ions present in the melt including the equilibrium with zirconium metal. Equilibrium electrode potentials of zirconium were measured in individual alkali chlorides (from lithium to cesium) and several mixtures (LiCl–KCl, NaCl–KCl, LiCl–CsCl), and the results obtained in the earlier works mostly employing stationary potentiometry techniques were reviewed by Smirnov [2]. Anodic and cathodic processes were studied by galvanostatic polarization method in zirconium containing melts based on the equimolar mixture of sodium and potassium chlorides [3,4]. Currently much attention is paid to studying zirconium electrochemistry in 3LiCl–2KCl eutectic based melts because this electrolyte is considered for the large scale pyrochemical SNF reprocessing. Electrorefining in molten salts was also considered as a possible mean of separating zirconium from irradiated fuel rods cladding (zirconium-based alloys) [5–8]. Transient electrochemical techniques (cyclic voltammetry being the most popular) were employed to characterize zirconium behavior but there is no full agreement in interpreting the experimental data [7–12]. It is generally agreed that zirconium in 3LiCl–2KCl based melts (around 500 °C) can present in two soluble ( $\text{Zr}^{4+}$ ,  $\text{Zr}^{2+}$ ) and two insoluble ( $\text{ZrCl}$ , Zr) forms. From two to four oxidation waves and two or three reduction waves were reported on the cyclic voltammograms, each wave being assigned to a particular redox reaction [7–10].

In the absence of oxygen uranium in molten chloride systems can form the ions in the oxidation states +3 and +4. The electrochemical behavior of uranium species in alkali chloride-based melts was studied in sufficient detail. Analysis of the results of potentiometric measurements performed on solid electrodes for U/(U(III)) and U(III)/U(IV) red-ox couples and reported by various researchers showed very good agreement [13].

Active (solid or liquid) metal electrodes can be used to alter deposition potentials due to formation of alloys or stable intermetallic compounds with deposited metal. Choosing appropriate electrode material can improve selectivity of the deposition process and increase separation of metals with close electrochemical properties. Various metals, normally with low melting points, are used as so-called “active” liquid cathodes. Electrochemistry of uranium on various liquid metal electrodes in chloride melts was studied [14–16] but substantially less attention was paid to reduction of zirconium chloro-species on liquid metals. Cyclic and differential pulse voltammetry was previously employed for assessing zirconium deposition on various liquid cathodes including gallium, indium and zinc [17–19]. A positive shift of zirconium deposition potential was observed on liquid “active” electrodes compare to an “inert” solid tungsten electrode due to formation of intermetallic compounds. Potentiostatic electrolysis on a zinc cathode at  $-(1.9\text{--}2.2)$  V vs.  $2\text{Cl}^-/\text{Cl}_2$  reference couple yielded  $\text{Zn}_{22}\text{Zr}$  phase [20]. Preliminary studies showed that cathodic polarization measurements could provide a valuable insight into zirconium and uranium deposition behavior on liquid metal cathodes [18,19]. Analysis of the polarization curves

allowed determining the potentials at which the cathodic reactions took place, including  $U^{4+} \rightarrow U^{3+}$ ,  $U^{3+} \rightarrow U^0$  and  $Zr^{n+} \rightarrow Zr^0$  reduction and evaluating applicability of various materials for separation of these two metals. The present study was primarily aimed at application of cathodic polarization measurements for determining the effect of the electrode material on the deposition potentials of uranium and zirconium in order to select the electrode with increased difference of deposition potentials for enhancing possible Zr/U separation factor.

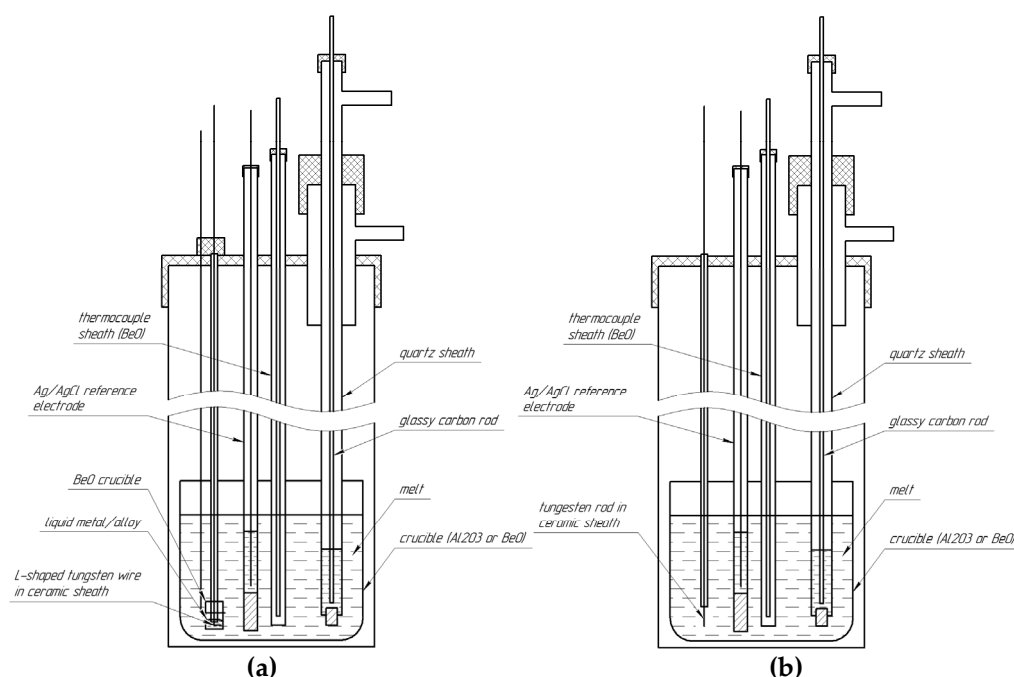
## 2. Materials and Methods

Cyclic, differential pulse or square wave voltammetry are often employed for determining deposition potentials of various metals in fused salt electrolytes. These techniques belong to transient electrochemical methods, while stationary (galvanostatic or potentiostatic) electrolysis is used in practical applications. Electrode polarization is one of such stationary methods. Polarization technique involves measuring the electrode potential at the moment of switching off polarizing current of a certain value passed through the system for a given period of time. Repeated measurements at various current values allow constructing polarization curves that characterize stationary dependence of the electrode potential on current density. This technique provides reliable data concerning stages of the electrode processes, metal deposition potentials, etc. The method involves cyclic alteration of periods of applying and switching off current with a gradual increase of the current values according to a logarithmic law. A necessary requirement for obtaining reproducible results is attaining in each polarization cycle a stationary state, when the working electrode potential reaches a stationary value.

The experiments were performed in the melts based on the 3LiCl–2KCl eutectic mixture. Anhydrous lithium and potassium chlorides were first dried under vacuum at 300 °C for 2–3 h and then melted. Gaseous hydrogen chloride was bubbled through molten salts for 2–3 h to convert any oxide impurities to chlorides. Then molten salts were kept under vacuum to remove dissolved HCl. Individual chlorides thus prepared were poured into alumina crucibles, cooled and stored in an argon filled glove box (Glovebox Systemtechnik GmbH, Malsch, Germany, <1 ppm O<sub>2</sub>, <0.1 ppm H<sub>2</sub>O). The eutectic mixture of lithium and potassium chlorides was prepared by fusing the salts in the required proportion. Melts containing zirconium and uranium chlorides were obtained by dissolving a desired amount of anhydrous ZrCl<sub>4</sub>, UCl<sub>4</sub> or UCl<sub>3</sub>. Commercially available zirconium tetrachloride was used. Uranium tetrachloride was prepared by reacting uranium trioxide with hexachloropropene following a standard procedure [21]. Uranium trichloride was then produced by reducing UCl<sub>4</sub> with metallic zinc. Resulting UCl<sub>3</sub> was purified from excess zinc, zinc chloride and unreacted uranium tetrachloride by heating under vacuum. Prepared uranium and zirconium containing salts were kept and handled in the glove box.

Three-electrode cells were used for studying cathodic polarization in uranium and zirconium containing melts. Construction of the cells employed for the measurements involving solid and liquid metal cathodes is schematically presented in Figure 1. Solid working electrode was made of a tungsten rod (1.7–2 mm dia.) sheathed by alumina or beryllium oxide ceramic tube to set a specific surface area. Liquid metal working electrodes were constructed of small beryllium oxide crucibles (ca. 6–8 mm i.d.) holding the low melting metals or alloys. These crucibles were attached to molybdenum wire supports to hold them in place (Figure 1). Thin tungsten wire (0.5 mm) acted as a current conductor to the liquid metal. Low end of the wire was bent under 90 degrees (L-shaped) to provide the contact with liquid metal, and vertical part was sheathed by a thin ceramic capillary tube (Al<sub>2</sub>O<sub>3</sub> or BeO) to isolate it from the contact with molten salt electrolyte. Pure gallium, zinc, as well as Ga–Sn (13.5 wt. % Sn), Ga–Zn eutectic (3.64 wt. % Zn, m.p. 25.5 °C), Ga–In eutectic (21.8 wt. % In, m.p. 16 °C) alloys were used as low melting metal electrodes. The reference electrode consisted of a silica tube closed from the end by a diaphragm. This tube contained silver wire dipped into 1 mol. % solution of silver chloride in NaCl–2CsCl eutectic. Known temperature dependence of silver electrode potential in NaCl–2CsCl

based melts was used to convert the potential values thus measured to  $2\text{Cl}^-/\text{Cl}_2$  couple (standard chlorine reference electrode). The counter electrode (anode) consisted of a silica tube closed from the bottom by a diaphragm. The tube contained 3LiCl–2KCl eutectic mixture and a glassy-carbon rod, and had a side-arm in the upper part to let chlorine evolved during the polarization measurements to escape. The temperature was measured by a K-type thermocouple dipped into the melt in a beryllium oxide sheath.



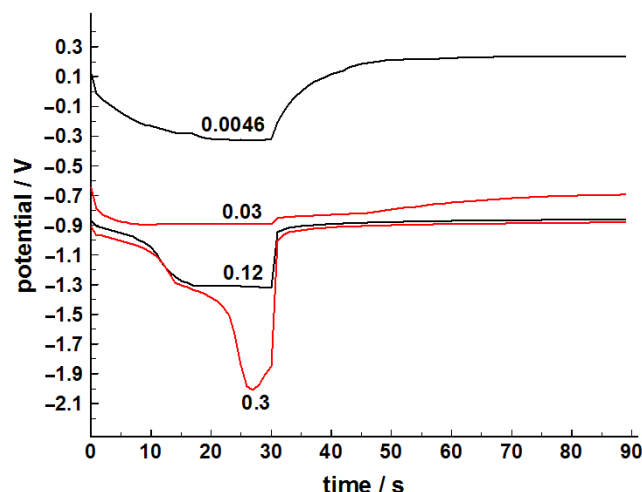
**Figure 1.** Experimental cells for studying polarization of liquid (a) and solid (b) metal cathodes in LiCl–KCl based melts.

The electrochemical measurements were conducted using an Autolab PGSTAT 302N potentiostat/galvanostat (Metrohm AG, Herisay, Switzerland). Prior to applying polarizing current a necessary time was allowed for the electrode potential to reach a stationary value. Then a constant cathodic current was passed through the system followed by a currentless pause. In a preliminary series of experiments the duration of applying polarizing current was chosen at 30 s and duration of the subsequent currentless pause at 60 s. Polarizing current was gradually increased from 0.0001 to 1 A. Working electrode potential value used for constructing the polarization curve was recorded 0.1 s after switching off polarizing current.

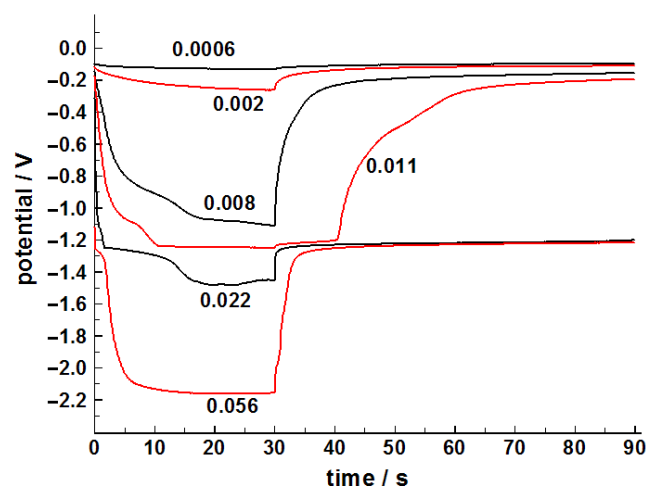
### 3. Results and Discussion

Previous studies involving cyclic and differential pulse voltammetry measurements in zirconium and uranium chloride containing melts showed that the nature of the working electrode had the effect on the potential at which uranium and zirconium ions were reduced to the metallic state [17,18,22]. This work was aimed at more in depth studying the electroreduction processes by galvanostatic polarization technique.

Examples of the potential–time dependencies recorded after applying and switching off polarizing current in zirconium and uranium containing melts are presented in Figures 2 and 3, respectively. Depending on the cathodic current density potentials were stabilized at certain values corresponding to particular electrochemical processes.



**Figure 2.** Examples of chronopotentiograms recorded during cathodic polarization of tungsten electrode in 3LiCl–2KCl–ZrCl<sub>4</sub> melts (2.14 wt. % Zr, 532 °C). Polarization current density (A/cm<sup>2</sup>) is given on the graph for each set of data. Potentials vs. Ag/AgCl reference electrode.

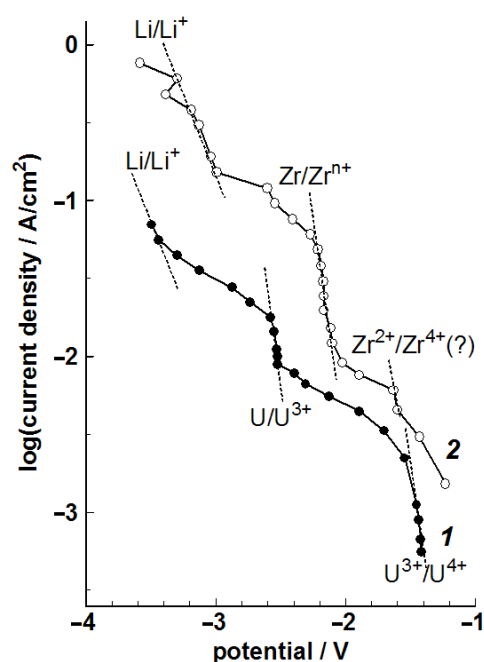


**Figure 3.** Examples of chronopotentiograms recorded during cathodic polarization of tungsten electrode in 3LiCl–2KCl–UCl<sub>3</sub> melts (1.14 wt. % U, 546 °C). Polarization current density (A/cm<sup>2</sup>) is given on the graph for each set of data. Potentials vs. Ag/AgCl reference electrode.

The chronopotentiogram recorded in a 3LiCl–2KCl–ZrCl<sub>4</sub> melt at low current densities (i.e., 0.0046 A/cm<sup>2</sup> in Figure 2) corresponded to the reduction of Zr<sup>4+</sup> to Zr<sup>n+</sup> ( $n = 2$  or  $3$ ) ions. Increasing current density shifted the potential to the cathodic region and the chronopotentiograms obtained at 0.03 and 0.12 A/cm<sup>2</sup> current densities (Figure 2) corresponded to reduction of zirconium ions to metallic zirconium. At higher current densities reduction of Li<sup>+</sup> ions took place (cf. the chronopotentiogram recorded at 0.3 A/cm<sup>2</sup> current density in Figure 2). Somewhat similar picture was observed in uranium containing melts. The chronopotentiograms presented in Figure 3 and recorded at low current densities corresponded to reduction of U<sup>4+</sup> to U<sup>3+</sup> ions (uranium(IV) was present as a minor impurity in the melt as discussed below). Increasing current density led to uranium deposition (e.g., as shown in Figure 3 by the chronopotentiogram recorded at 0.022 A/cm<sup>2</sup> current density) and ultimately to reduction of lithium ions, similar to zirconium containing melts.

Examples of cathodic polarization curves obtained on a solid tungsten electrode in chloride melts containing zirconium or uranium ions are presented in Figure 4. Cathodic polarization curve recorded in the zirconium containing melt had two regions of potential stabilization, around  $-2.1$  and  $-3.2$  V vs. 2Cl<sup>−</sup>/Cl<sub>2</sub> reference couple. First potential corresponded to the reduction of zirconium ions to the metal. Zirconium deposition

potentials obtained on tungsten cathodes were  $-(2.05\text{--}2.10)$  V at  $532\text{--}544$  °C and zirconium concentration in the melt of 2.14 wt. %. These values agree well with the results obtained previously using transient techniques [17].

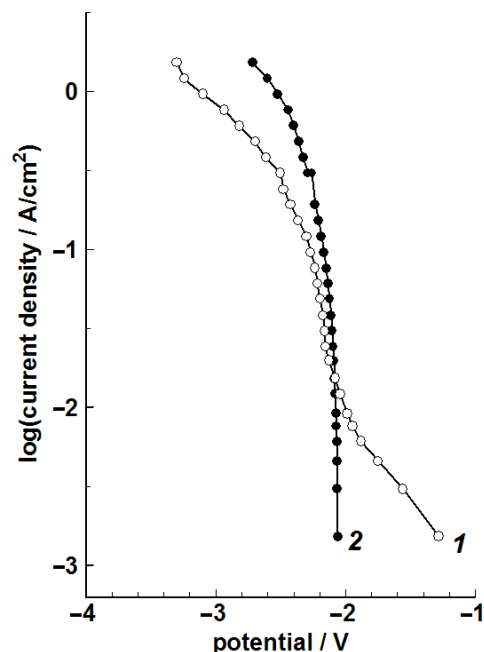


**Figure 4.** Cathodic polarization curves of tungsten electrode in 3LiCl–2KCl eutectic based melts containing 1.65 wt. %  $\text{UCl}_3$  at  $546$  °C (1) or 5.47 wt. %  $\text{ZrCl}_4$  at  $532$  °C (2). Potentials vs.  $2\text{Cl}^-/\text{Cl}_2$  reference couple.

Increasing temperature shifted the reduction potential to slightly more positive values, Figure 5. Limiting current density for zirconium deposition was around  $0.08\text{--}0.15$  A/cm<sup>2</sup>. At higher current densities co-reduction of zirconium and alkali metal (lithium) ions took place and the potential shifted further to negative values until reached the potential of lithium deposition  $-(3.1\text{--}3.3)$  V, and this was reflected by the second region of potential stabilization on the polarization curves. There was no other clearly defined regions of potential stabilization observed on the polarization curves recorded in zirconium containing melts at the potentials more positive than  $-2$  V that could be attributed to the reduction of Zr(IV) ions to lower oxidation states. Cyclic voltammetry measurements showed that reduction of Zr(IV) ions occurred in several stages. The cathodic reduction peaks in 3LiCl–2KCl based melts were observed around  $-1.75$ ,  $-2.20$  and  $-2.56$  V (vs.  $2\text{Cl}^-/\text{Cl}_2$  reference couple) and attributed to the formation of Zr(II) ions, deposition of zirconium monochloride and zirconium metal [10,17]. There is an indication of a possible potential stabilization at ca.  $-1.6$  V (curve 2 in Figure 4) that can be associated with Zr(IV) to Zr(II) reduction.

Cathodic polarization curves recorded in uranium containing melts had three regions of the potential stabilization around  $-1.4$ ,  $-2.5$  and  $-3.3$  V vs.  $2\text{Cl}^-/\text{Cl}_2$  reference couple. These correspond to reduction of U(IV) to U(III) ions, U(III) to uranium metal and reduction of lithium ions. Potentials for U(III)/U(IV) and U(0)/U(III) couples corresponded to the expected values and agree well with the literature [13]. The region of potential stabilization corresponding to U(IV) to U(III) reduction was observed even in the melts prepared by dissolving uranium trichloride, although the limiting current density for this reduction was rather small, ca.  $0.001$  A/cm<sup>2</sup>. This indicates that 3LiCl–2KCl– $\text{UCl}_3$  melts contained small impurity of U(IV) chloride resulting either from incomplete purification of  $\text{UCl}_3$  samples from unreduced  $\text{UCl}_4$  or formed when  $\text{UCl}_3$  was fused with 3LiCl–2KCl eutectic.





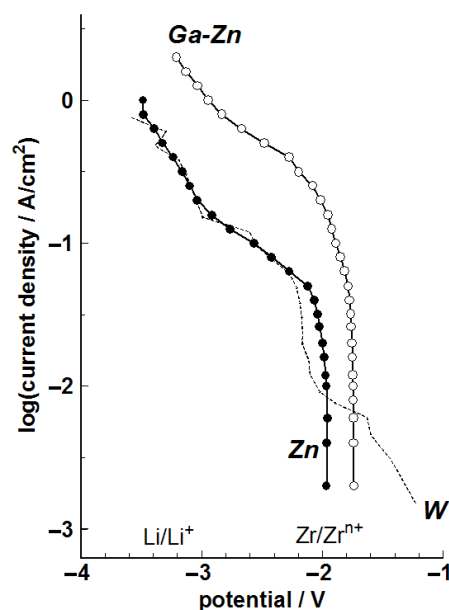
**Figure 5.** Cathodic polarization curves of tungsten electrode in 3LiCl–2KCl eutectic based melts containing 5.47 wt. % ZrCl<sub>4</sub> at 544 °C (1) and 637 °C (2). Potentials vs. 2Cl<sup>−</sup>/Cl<sub>2</sub> reference couple.

The difference of deposition potentials for uranium and zirconium on the solid tungsten electrode was around 0.4 V. Increasing temperature shifts the electrode potential to more positive values but would not alter much the difference of the deposition potentials for two metals. Material of the cathode can have a noticeable effect on the deposition potential. Cyclic and differential pulse voltammetry experiments showed that using gallium, indium or zinc electrodes allowed shifting zirconium deposition potential to more positive values [17,18]. Maximum positive shift of the potential, ca. 0.2 V, was observed on gallium and indium electrodes. From the other side zinc was proposed as a promising material for separating uranium and zirconium using potentiostatic pulse electrolysis [23]. Compare to zinc, gallium and indium has the disadvantage of higher cost and very low vapor pressure at elevated temperatures. The latter makes challenging further separation of these metals from the alloys with zirconium for recycling.

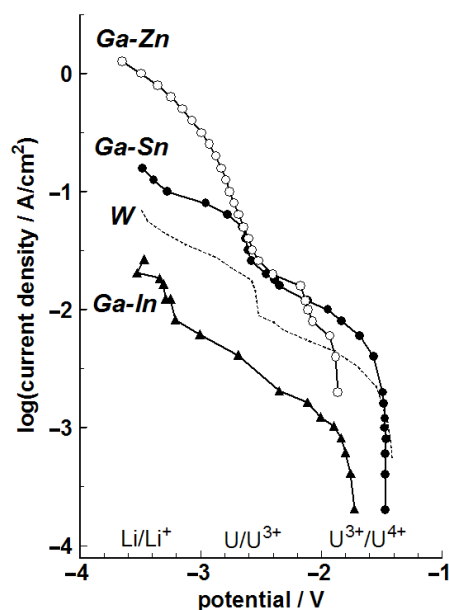
Zinc and gallium–zinc eutectic alloy were tested as the cathode materials for the reduction of zirconium. Cathodic polarization curves obtained for liquid Zn and Ga–Zn electrodes in 3LiCl–2KCl–ZrCl<sub>4</sub> melts are presented in Figure 6. The results for solid tungsten electrode are included in the figure for comparison. Polarization curves recorded on liquid cathodes had clear potential stabilization regions around  $-(1.7\text{--}2.0)$  V corresponding to zirconium reduction and below  $-3$  V corresponding to alkali metal reduction. Zirconium deposition potentials thus obtained were  $-1.97$  V for zinc (567 °C) and  $-1.74$  V for Ga–Zn alloy (550 °C). Changing from tungsten to zinc thus resulted in ca. 0.13 V positive shift of zirconium deposition potential. Gallium–zinc alloy demonstrated the most positive zirconium deposition potential value of  $-1.74$  V, i.e., 0.35 V more positive than on tungsten, making this alloy an interesting candidate material for uranium and zirconium separation.

To study the effect of the electrode material on reduction potential of uranium, cathodic polarization measurements were performed in LiCl–KCl–UCl<sub>3</sub> melts. Low melting alloys of gallium with tin, zinc and indium were used as the cathode materials. Polarization curves recorded on various cathodes are presented in Figure 7. Similar to the results obtained on the solid tungsten electrode, first region of the potential stabilization on the polarization curves around  $-(1.4\text{--}1.8)$  V corresponded to the reduction of U(IV) to U(III) ions. Reduction of U(III) ions (second region of the potential stabilization) was observed around  $-(2.5\text{--}2.6)$  V for Ga–Sn and Ga–Zn alloys. These values are very close to the

uranium deposition potential value of  $-2.52$  V, found from the polarization measurements on the solid tungsten electrode. The polarization curve recorded on Ga–In eutectic alloy cathode did not exhibit a clear potential stabilization for U(III) to uranium metal reduction. Aluminum containing alloys were proposed as possible working media for separating uranium and zirconium [24–26]. Attempts to record polarization curves in uranium containing chloride melts on gallium–aluminum alloy cathodes were unsuccessful. It is likely that aluminum reacted with uranium ions in the salt electrolyte reducing them to the metal. Compatibility of aluminum with uranium containing chloride melts remains a matter of certain controversy and requires further investigation [16,27,28].



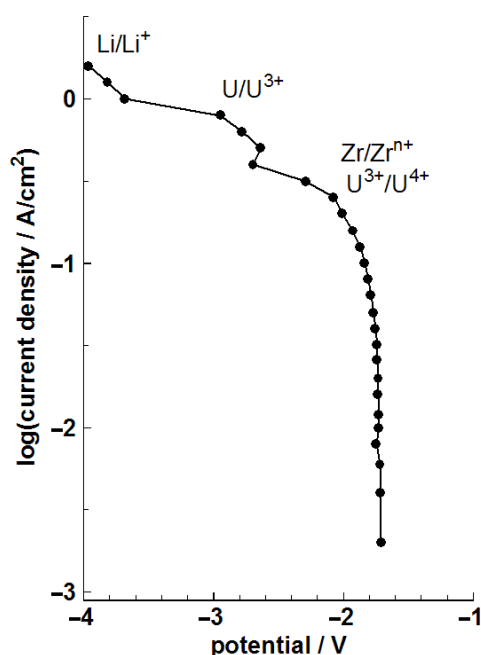
**Figure 6.** Polarization of liquid Zn and Ga–Zn cathodes in  $3\text{LiCl}-2\text{KCl}-\text{ZrCl}_4$  melts at  $567^\circ\text{C}$  (0.89 wt. %  $\text{ZrCl}_4$ ) and  $550^\circ\text{C}$  (0.87 wt. %  $\text{ZrCl}_4$ ), respectively. Potentials vs.  $2\text{Cl}^-/\text{Cl}_2$  reference couple. Polarization curve for solid tungsten cathode is shown for comparison.



**Figure 7.** Polarization of liquid Ga–Zn, Ga–Sn and Ga–In cathodes in  $3\text{LiCl}-2\text{KCl}$  based melts containing uranium chloride at  $541^\circ\text{C}$  (2.08 wt. %  $\text{UCl}_3$ );  $596^\circ\text{C}$  (0.90 wt. %  $\text{UCl}_3$ ) and  $550^\circ\text{C}$  (0.90 wt. %  $\text{UCl}_3$ ), respectively. Potentials vs.  $2\text{Cl}^-/\text{Cl}_2$  reference couple. Polarization curve for solid tungsten cathode is shown for comparison.



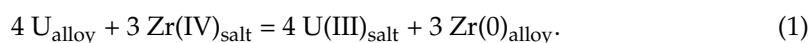
Thus, the low melting cathodes used in the present study did not show an appreciable effect on uranium deposition potential. Based on the results obtained for zirconium, Ga–Zn eutectic was tested as a possible base alloy for uranium and zirconium separation. A polarization curve recorded on the Ga–Zn eutectic alloy cathode in  $3\text{LiCl}-2\text{KCl}-\text{ZrCl}_4-\text{UCl}_4$  melt is presented in Figure 8. In agreement with the previous findings reduction of U(IV) ions U(III) and zirconium ions to zirconium took place at very close potentials, as shown by the first region of potential stabilization in Figure 8. Reduction of U(III) ions to metallic uranium occurred around  $-2.7\text{ V}$  and the current densities were over  $0.4\text{ A/cm}^2$ . Thus, there was a noticeable difference in the deposition potentials of zirconium and uranium on the Ga–Zn eutectic alloy cathode. Therefore it can be assumed that such cathode would allow deep separation of these two metals.



**Figure 8.** Polarization of liquid Ga–Zn alloy cathode in  $3\text{LiCl}-2\text{KCl}-\text{ZrCl}_4-\text{UCl}_4$  melt at  $534\text{ }^{\circ}\text{C}$  (1.64 wt. %  $\text{ZrCl}_4$ , 2.03 wt. %  $\text{UCl}_4$ ). Potentials vs.  $2\text{Cl}^-/\text{Cl}_2$  reference couple.

Processes of separating two metals by selective cathodic reduction or by an exchange red-ox reaction (e.g., reductive extraction) are of the same nature. Therefore the maximum possible (thermodynamically achievable) effectiveness of a separation process can be deduced applying any of these approaches. Here, to estimate the effectiveness of a separation process for uranium and zirconium using a given “molten salt—liquid metal” system, thermodynamically achievable Zr/U separation factors were determined under stationary conditions. The system considered involved  $3\text{LiCl}-3\text{KCl}-\text{ZrCl}_4-\text{UCl}_3$  salt melt and a liquid metal alloy containing zirconium and uranium. The alloys were based on gallium–zinc eutectic and pure gallium (for comparison) and the experiments were conducted in the following manner. A sample of a Me–U–Zr alloy (where Me = Ga or Ga–Zn) was held in contact with  $3\text{LiCl}-2\text{KCl}-\text{UCl}_3-\text{ZrCl}_4$  salt melt under static conditions (without stirring) at a constant temperature. The course of the reaction was followed by recording the potential of the liquid alloy. Compositions of the salt and metallic phases used in the experiments prior and after the contact are listed in Table 1.

Amount of uranium dissolved from the metallic phase and zirconium left the salt melt agreed with the stoichiometry of the expected exchange reaction:



**Table 1.** Composition of the salt melt and metallic alloy in the experiment on assessing U/Zr separation factor in a “molten salt—liquid metal” system.

Element	Initial Concentration (wt. %)		Final Concentration (wt. %)		Distribution Coefficient	Zr/U Separation Factor
	3LiCl–2KCl Melt	Alloy	3LiCl–2KCl Melt	Alloy		
Ga based alloy, 533 ± 2 °C, 6 h						
U	0.581	11.458	1.02	0.0461	0.045	800
Zr	0.286	2.537	0.1435	5.18	36.1	
Ga–Zn eutectic based alloy, 540 ± 2 °C, 29 h						
U	0.568	12.060	1.23	0.10	0.081	2590
Zr	0.275	2.663	0.029	6.08	209.7	

Distribution coefficients ( $K_d$ ) were calculated as the ratio of uranium or zirconium concentrations in the metallic and salt phases after equilibrating.  $K_d(\text{U})$  were below unity and  $K_d(\text{Zr})$  above unity. Zirconium-uranium separation factors were calculated from the ratio of the corresponding distribution coefficients. The values of thermodynamically possible separation factors were 800 for gallium and 2590 for Ga–Zn eutectic alloy. The latter value confirmed that the liquid cathode based on Ga–Zn eutectic can be effectively used for separating uranium and zirconium.

#### 4. Conclusions

Polarization of solid inert (tungsten) and liquid active cathodes in chloride melts containing uranium and zirconium was studied aiming to select a suitable electrode material for sufficiently deep separation of uranium and zirconium in a pyrochemical process of spent nuclear fuels reprocessing. The nature of the working electrode (tungsten, gallium–zinc, gallium–tin and gallium–indium alloys) had little effect on the uranium deposition potential values. A different behavior was observed in zirconium containing systems. Deposition of zirconium on Ga–Zn eutectic alloy took place at ca. 0.35 V more positive potential than on tungsten thus providing the electrode material with a large potential difference of uranium and zirconium deposition. Thermodynamically possible Zr/U separation factors were experimentally determined for gallium and gallium–zinc based alloys, and confirmed higher efficiency of Ga–Zn alloy for separating zirconium and uranium. The value of the separation factor obtained under static conditions in a “chloride melt—liquid alloy” system at ca. 540 °C was 2590 for Ga–Zn compare to 800 for Ga based alloys.

**Author Contributions:** Conceptualization, V.A.V. and D.S.M.; methodology, V.A.V.; validation, V.A.V. and M.N.S.; formal analysis, D.S.M. and M.N.S.; investigation, V.A.V., M.N.S., A.A.R. and A.B.I.; resources, V.A.V.; data curation, V.A.V. and D.S.M.; writing—original draft preparation, V.A.V.; writing—review and editing, V.A.V. and A.A.R.; visualization, A.A.R. and A.B.I.; supervision, V.A.V.; project administration, D.S.M. and A.A.R.; funding acquisition, D.S.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** The study was supported by the Russian Science Foundation, project no. 17-73-20156.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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